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Modeling of electron-vibrational $4f^n$–$4f^{n-1}5d$ spectra in $LiYF_4:RE^{3+}$ crystals

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Abstract

In the present work, the low temperature absorption band shapes of the impurity Ce^{3+} (4f–5d) and Lu^{3+} ($4f^{14}$–$4f^{13}5d$) ions in $LiYF_4$ crystals have been simulated within adiabatic approximation on the basis of a derived microscopic model of electron–phonon interaction and phonon spectrum of the host lattice. Crystal field parameters and electron–phonon coupling constants were treated in the framework of the exchange charge model. Results of simulations of the spectral envelopes agree satisfactorily with the experimental data available from the literature.

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Keywords: 4f–5d spectra; Electron–phonon interaction; $LiYF_4$

1. Introduction

In the past, the interconfigurational $4f^n$–$4f^{n-1}5d$ transitions in rare earth (RE) ions have not received much attention, lying generally in the vacuum-ultraviolet (VUV) region and being experimentally less accessible, than intraconfigurational $4f^n$ transitions. Besides, most of the intensity in the $4f^n$–$4f^{n-1}5d$ transitions is in broad vibronic bands with widths up to a thousand of wave numbers even at liquid helium temperature making the spectra more difficult to analyze.

In recent years, however, there has been a considerable interest in VUV spectra of RE compounds as part of effort to design new efficient VUV phosphors and scintillator materials. Both absorption and emission spectra for $4f^n$–$4f^{n-1}5d$ transitions have been obtained for most RE ions in several host crystals [1,2]. $LiYF_4$ is an example of crystal with intermediate electron-lattice coupling in 4f–5d transitions in doping RE ions when along wide vibronic bands the narrow phonon lines are observed.

Theoretical modeling of energy level patterns and transition intensities in the $4f^n$–$4f^{n-1}5d$ spectra were carried out for a lot of systems [1,2]. Vibronic bands, however, are usually approximated as Gaussian, with three adjustable parameters: the offset, the bandwidth and the intensity ratio of the zero-phonon line (ZPL) to the vibronic band.

The goal of the present work is to establish a microscopic model of electron–phonon interaction, operating with the real phonon spectrum of the host crystal lattice, and simulate uniformly the energy level structure and the electron-vibrational band lineshapes.

The low temperature absorption band shapes of the impurity Ce^{3+} (4f–5d) and Lu^{3+} ($4f^{14}$–$4f^{13}5d$) ions in $LiYF_4$ crystals have been simulated and compared with available experimental data.

2. Simulation of $4f^n$– $4f^{n-1}5d$ spectra in the adiabatic approximation

Energy levels and wave functions for the ground ($4f^n$) and excited ($4f^{n-1}5d$) electronic configurations of RE^{3+} ions were obtained from numerical diagonalization of the

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